PATENT ABSTRACTS OF JAPAN

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(54) BLOCK TERPOLYMER AND METHOD FOR PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an aromatic vinyl-butadiene block copolymer having excellent mechanical characteristics, capable of being easily controlled in relative amounts of constituents contained in the block copolymer, and capable of realizing suitable physical characteristics brought about by controlling the constituents.

SOLUTION: This block terpolymer comprises a copolymer with five polymer blocks, has a molecular weight of 50,000-400,000, and is expressed by formula (1): pS-pI-pB-pI-pS (pS is an aromatic vinyl polymer; pB is a butadiene polymer; and pI is an isoprene polymer), wherein the pB has a 1,4-structure in an amount of ≥ 70%, the pS is contained in an amount of 5-50%, and the pB and the pI are contained in amounts so as to satisfy: (pB/pI)≥1. The copolymer has high tensile strength, because the copolymer has such a structure that the isoprene polymer blocks are inserted between the styrene polymer blocks and the butadiene polymer block. Further, contents of the constituents are controllable, so that the suitable physical characteristics for use of the copolymer is realized.

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CLAIMS

[Claim(s)]
[Claim 1]
It is 5-fold block copolymer, and it appears by the following formula (1) and the molecular weight in the following type is 50,000-400,000. It is the 3 yuan block copolymer which 1 and 4 structure of pB is 70% or more, and the content of pS is 5 - 50%, and is characterized by the content of pB and pI being pB/pI>=1 in a weight ratio.
pS-pI-pB-pI-pS (1)
However, by the formula, pS is a vinyl aromatic series polymer, pB is a butadiene polymer, and pI is an isoprene polymer.
[Claim 2]
The above-mentioned vinyl aromatic series polymer is a 3 yuan block copolymer according to claim 1 characterized by being the polymer of an one or more sort monomer chosen from the group which consists of styrene, alpha methyl styrene and o-methyl styrene, p-methyl styrene, and p-tert-butyl styrene.
[Claim 3]
The above-mentioned vinyl aromatic series polymer is a 3 yuan block copolymer according to claim 1 characterized by being the polymer of styrene.
[Claim 4]
The content of the above-mentioned vinyl aromatic series polymer is a 3 yuan block copolymer according to claim 1 characterized by being 5 - 35 % of the weight.
[Claim 5]
The molecular weight of the above-mentioned vinyl aromatic series polymer is claim 1 characterized by being the range of 8,000-20,000 thru/or a 3 yuan block copolymer given in four.
[Claim 6]
Phase which uses an organic lithium initiator with a non-active hydrocarbon system solvent, carries out a polymerization until it adds a vinyl aromatic series monomer and a negatively accelerated phosphorescence is carried out, and compounds a living polymerization object;
until it adds an isoprene monomer on the above-mentioned living polymerization object and a negatively accelerated phosphorescence is carried out to it -- a polymerization -- carrying out -- a jib -- phase; which compounds a lock living polymerization object
the above-mentioned jib -- phase; which carries out a polymerization until it adds a butadiene monomer on a lock living polymerization object additionally and a negatively accelerated phosphorescence is carried out to it, and compounds a triblock living polymerization object -- and
How to manufacture the 3 yuan block copolymer characterized by consisting of phases of adding a binder on the above-mentioned triblock living polymerization object, and carrying out a coupling reaction.
[Claim 7]
It is the manufacture approach of the 3 yuan block copolymer according to claim 6 characterized by using the mixture of a cyclohexane, a cyclohexane, and n-hexane, and the mixture of a cyclohexane and n-heptane as the above-mentioned non-active hydrocarbon system solvent.
[Claim 8]
It is the manufacture approach of the 3 yuan block copolymer according to claim 6 characterized by using n-butyl

lithium or sec-butyl lithium as the above-mentioned organic lithium initiator.
[Claim 9]
The above-mentioned binder is the manufacture approach of the 3 yuan block copolymer according to claim 6 characterized by being a binder with two or more joint functional groups.
[Claim 10]
The above-mentioned binder is the manufacture approach of the 3 yuan block copolymer according to claim 6 characterized by being one or more binders chosen from the group which consists of dichlorodimethylsilane, a dichloro diphenyl silane, and tetra-chlorosilicane.
[Claim 11]
The rate of coupling of the above-mentioned coupling reaction is the manufacture approach of the 3 yuan block copolymer according to claim 6 characterized by being 50 - 100% of range.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[Field of the Invention]
[0001]
This invention relates to a vinyl aromatic series polymer and the block copolymer which has the structure where the isoprene block was added by the butadiene polymer block about the block copolymer which consists of a vinyl aromatic series polymer and a butadiene polymer. The physical-properties embodiment as a thermoplastic elastic body is related with the structure and its manufacture approach of an easy block copolymer by relative content accommodation of a block copolymer in more detail about the block copolymer of the vinyl aromatic series polymer whose mechanical strength improved, and a butadiene polymer.
[Background of the Invention]
[0002]
Generally the styrene system block copolymer (Styrenic Block Copolymer) which consists of a giant-molecule block of a vinyl aromatic series monomer and a conjugated diene giant-molecule block has the structure of 3-fold block or a double block, and has the property of a thermoplastic elastic body. It can be said that SBS (polystyrene-block-polybutadiene-block-polystyrene) obtained when a butadiene is used as an inside [this] conjugated diene monomer is the typical macromolecule of a styrene system block copolymer (SBC, styrenic block copolymer). SBS has 3-fold block structure which consists of a styrene polymer block which is a hard giant molecule, and a butadiene polymer block which is an elasticity giant molecule with high elasticity, and such a structural description offers high application. Two sorts of polymer blocks are not mixed with each other, detailed phase separation is made, and such a phenomenon of a block copolymer is distinguished from the phase separation generated in general macromolecule mixing from the point that between blocks consists of covalent bond. That is, a main block is an elastic body giant molecule, and it will have the configuration connected with the giant-molecule chain of the main block which has elasticity between the strong letters of isolation which the giant-molecule block of both ends forms completely by having the giant-molecule block of the letter of isolation in both. Therefore, this high polymer will have the thermoplasticity and the mechanical strength which the giant molecule which forms the letter of isolation offers, and the elastic body giant molecule which is a main block will have in coincidence the elasticity which can store mechanical stress to a giant-molecule chain. Therefore, SBS is used for wide range applicable fields, such as modified asphalt, compounding, shoes components, and adhesives, as a thermoplastic elastic body which has the property of thermoplastics, and the property of an elastic body in coincidence. On the other hand, SIS (polystyrene-block-polyisoprene-block-polystyrene) of 3-fold block structure acquired from a styrene polymer and an isoprene polymer is mainly used as a material of a binder or adhesives.
[0003]
The block copolymer of various structures is shown about styrene, the butadiene, and the 3 yuan copolymer that consists of an isoprene. It is shown to the American patent No. 3,692,874 about the approach of introducing the block of a butadiene polymer into the block end of an isoprene polymer, and raising coupling effectiveness. Moreover, in No. 5,292,819 and No. 5,399,627, it has shown about the copolymer of the radial structure which appears by the formula of nX (n> 2) (pS-pI-pB). Especially the content of Pb block introduced in order to make coupling smooth has presented 5 or less % of the weight 10 or less % of the weight. If a coupling reaction is carried out for the polymer of an isoprene end by dichlorodimethylsilane under a benzene solvent according to the announced paper (53 JPS vol 36 1743- 1998),

it will be reported that 79% of coupling ratio is shown 20 hours after. According to this paper, the steric hindrance effectiveness of a reaction end was taken up as a key factor child who affects a coupling ratio. In the case of the isoprene, the steric hindrance effectiveness by the methyl group of an end interpreted it as it being large and the ratio of coupling being low compared with the butadiene. In this case, in order to raise coupling effectiveness, a little butadiene block is merely added and the overall elastic body effectiveness is acquired from an isoprene block. Therefore, the block copolymer obtained in this way has the physical properties of SIS which consist of a block of a styrene polymer and an isoprene polymer fundamentally.

[0004]

Moreover, in order to raise thermal stability, there is an example which introduced both the isoprene block and the butadiene block. Generally, since crosslinking reaction occurs at an elevated temperature, viscosity increases a butadiene macromolecule, and if an isoprene macromolecule is heated, viscosity will decrease along with association between atoms being disassembled. Therefore, there is an example shown about the approach which the viscosity change in an elevated temperature is offset and raises thermal stability by introducing both an isoprene block and a butadiene block.

[0005]

In American JP,4,120,915,B, it has shown about the block copolymer which consists of the styrene which appears in S-D1-D2, conjugated diene, and the 2nd conjugated diene. It aims at improvement in thermal stability by introducing both blocks of a butadiene and the conjugated diene which appears in an isoprene. However, since this giant molecule is a resin giant molecule whose styrene content is 70% or more, the improvement in physical properties by such block installation has not been described. Moreover, it is characterized by having the molecular structure of the multiplex branch manufactured using a multiplex coupling agent.

[0006]

According to the American patent No. 5,532,319 and No. 5,583,182, the 3 yuan block copolymer of nX gestalt which introduces a butadiene block into a vinyl aromatic series-isoprene block copolymer, and is formed (S-B-I) was used, and the approach of preventing reduction of the viscosity by time amount at the time of manufacture of hot melt adhesive is shown by raising thermal stability.

[Patent reference 1] The American patent No. 3,692,874
[Patent reference 2] The American patent No. 5,292,819
[Patent reference 3] The American patent No. 5,399,627
[Patent reference 4] The American patent No. 4,120,915
[Patent reference 5] The American patent No. 5,532,319
[Patent reference 6] The American patent No. 5,583,182

[0007]

However, while the research to which research of most which made reference above adds a small amount of [at the end of a vinyl aromatic series-isoprene block copolymer] butadiene for an improvement of a coupling reaction rate and the improvement in thermal stability of a giant molecule at the time of manufacture of a vinyl aromatic series-isoprene block copolymer is most and adjusts the content of a vinyl aromatic series component, use of the isoprene for the mechanical improvement in physical properties of a vinyl aromatic series-butadiene block copolymer is not reported.

[0008]

As for the SBS product which turned quotient business, it is common to have about 30% of the weight of the styrene content. Since a mechanical strength will fall rapidly if there are few styrene contents than this, it can be said that the above-mentioned styrene content is the boundary point to which phase separation can happen effectively since it has a property as a thermoplastic elastic body. However, a styrene content affects mechanical physical properties, such as an index which affects the workability of a block copolymer, such as melt viscosity (melt viscosity) and solution viscosity (solution viscosity), tensile strength (tensile strength), and a degree of hardness (hardness). The material from which change of such physical properties etc. was called for by the application used, therefore the styrene content changed is called for. On the other hand, by SIS for which the isoprene was used instead of the butadiene, since the solubility constant difference between two components is large compared with the case of a vinyl aromatic series-butadiene, the vinyl aromatic series-isoprene block copolymer shows mechanical physical properties with the presentation of a vinyl aromatic series component sufficient [at least about 15 % of the weight]. According to the thermodynamic theory, the phase separation of a block copolymer is based on the common characteristic of the matter to block, the molecular

weight of a block copolymer, and the relative content of each component (Hamley, I.W., The Physics of Block Copolymers; Oxford University Press; Oxford, U.K.1998). A common characteristic is determined by the dissolution constant (solubility parameter) difference in the matter which forms a block. These three elements do not act in independent and determine overall phase separation with an interrelation. Therefore, changing the relative content of a component, effectiveness [satisfying / phase separation], i.e., in order to embody the physical properties of a thermoplastic elastic body as a result, it should adjust appropriately so that it may be compensated with the effectiveness by other elements, i.e., common characteristic, and molecular weight. After this invention performed consideration which has depth from such a viewpoint in the thermodynamic variable accompanying the phase separation effectiveness of a block copolymer, and it exerted on phase separation for suitable physical-properties embodiment, it is obtained.

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0009]

The purpose of this invention is for solving the above-mentioned trouble, and it sets it as the purpose to offer the vinyl aromatic series-butadiene block copolymer [mechanical physical properties are excellent, and / relative content accommodation of a block-copolymer constituent is easy, and] which can embody the suitable physical properties accompanying it.

[Means for Solving the Problem]

[0010]

the purpose of above this inventions is 5-fold block copolymer, and appears by the following formula (1) molecular weight is 50,000-400,000 and, for the inside pB of the following formula, 1 and 4 structure is 70% or more -- content of pS It is 5 - 50% and the content of pB and pI is attained by the 3 yuan block copolymer characterized by being pB/pI>=1 in a weight ratio.

pS-pI-pB-pI-pS (1)

However, by the formula, pS is a vinyl aromatic series polymer, pB is a butadiene polymer, and pI is an isoprene polymer.

[0011]

The block copolymer which this invention presents is characterized by having embodied the property as a thermoplastic elastic body whose mechanical physical properties has the structure of a 3 yuan block copolymer of the structure where the isoprene polymer block was added between the vinyl aromatic series polymer block and the butadiene polymer block, and improved according to the solubility constant difference between a vinyl aromatic series component and an isoprene polymer.

[Best Mode of Carrying Out the Invention]

[0012]

Hereafter, the block copolymer and its manufacture approach of this invention are explained.

The block copolymer which this invention presents is 5-fold block copolymer which appears by the formula of pS-pI-pB-pI-pS, pS is a vinyl aromatic series polymer, pB is a butadiene polymer, pI is an isoprene polymer, the range of molecular weight is 50,000-400,000, 1 and 4 structure of pB is 70% or more, and it is the content of a vinyl aromatic series polymer. It is 5 - 50% and the content of pB and pI is a block copolymer which is pB/pI>=1 in a weight ratio.

[0013]

The vinyl aromatic series polymer applied to this invention is a polymer of the styrene compound with which the alkyl group was permuted by aromatic series rings, such as styrene, alpha methyl styrene and o-methyl styrene, p-methyl styrene, and p-tert-butyl styrene. As a desirable vinyl aromatic series polymer, it is the polymer of styrene, alpha methyl styrene, and p-methyl styrene. It is the polymer of styrene still more preferably.

[0014]

A block copolymer will have the property of a thermoplastic elastic body by detailed phase separation. According to the theory, the phase separation of a block copolymer is influenced with molecular weight, the content of a block copolymer, and a common characteristic (chi). And a common characteristic is determined by the difference in the dissolution constant value (delta) of the polymer which constitutes each block as expressed to the following type (2).

chi 12=(delta1-delta2)2/RT >= 0 ..... (2)

[0015]

A common characteristic is a forward value, and the detailed phase separation of a block copolymer often happens, so that the difference in the dissolution constant value of two components is so large that [that is,] a common characteristic is large. According to the place where the dissolution constant value was known by reference, a styrene polymer is [8.38(cal/cm3) 1/1, and 4-isoprene polymer of 9.12(cal/cm3) 1/1, and 4-butadiene polymer] 8.22(cal/cm3) 1/2 about (Robert E.Cohen, D.E.Wilfong, Macromolecules, 1982, 15,370). [2 and 1] [2 and 1] Moreover, in 8.62 (cal/cm3) 1/2, and o-methyl styrene, 9.00(cal/cm3) 1/2, and p-methyl styrene have [alpha methyl styrene] the value of 9.00(cal/cm3) 1/2 (Husan Ahmed, M.Yassen, Polym.Eng.Sci., 1979, 19, 858). Therefore, the block copolymer which consists of styrene and an isoprene has the common index number of a larger value than the block copolymer which consists of styrene and a butadiene, and shows that it is still more advantageous to detailed phase separation. Therefore, the block copolymer which this invention presents is characterized by having the pS-pI-pB-pI-pS structure of a gestalt where pI block advantageous to phase separation was inserted between pS block and pB block in the block structure of SBS. The sequence of such a block is very important, and by inserting pI block between pS block and pB block, phase separation becomes easy and has the advantage to which the molecular weight which is other factors which this exerts on phase separation, and the relative content of a block polymer can be changed. Moreover, the physical-properties embodiment of a thermoplastic elastic body is effective at the result of effective phase separation, and especially the improvement in a mechanical strength can be expected.

[0016]

A butadiene polymer is large in the chemical structure, and is divided into 1 and 4-polybutadiene and 1 and 2-polybutadiene. Most has 1 and 4 structure and, as for the butadiene polymer manufactured by anionic polymerization, what is obtained in the content of 10% inside and outside [structure / 1 and 2] is common. However, the content may be increased by addition of amines (amine), such as the ether (ether) like a tetrahydro furan (tetrahydrofuran), or tetramethylethylenediamine (tetramethylethylenediamine). According to this invention, the content of 1 and 4 structure of desirable pB block is 70% or more.

[0017]

In order to insert an isoprene block and to make the physical properties of a styrene-butadiene block copolymer improve, there should be few contents of the isoprene polymer to contain than the content of a butadiene polymer. Therefore, as for the content of pI, 50% is not exceeded in whole pI and pB content which shows an elastic body property, but when a weight ratio shows, the desirable content of pB is pB/(pB+pI) >=0.5, or is shown by pB/pI>=1.

[0018]

It is the content of a vinyl aromatic series polymer with a 3 yuan block copolymer. Although it is applicable within 5 - 95%, the content of pS block which is a vinyl aromatic series polymer desirable for a suitable mechanical strength and an application is 5 - 50%, and is 5 - 35% range still more preferably. Although the molecular weight of a vinyl aromatic series polymer block does not need to be a specific value, in order to maintain mechanical physical properties and general melt nature, it is possible in the about 5,000 to 30,000 range, and is about 8,000 to 20,000 range preferably. The molecular weight of a 3 yuan block copolymer is possible in 50,000-400,000, and is the thing of 80,000-300,000 preferably.

[0019]

The manufacture approach of the block copolymer which this invention presents is 5-fold block copolymer, it appears in pS-pI-pB-pI-pS, and pS is a vinyl aromatic series polymer, pB is a butadiene polymer, and pI is an isoprene polymer, The range of molecular weight is 50,000-400,000, 1 and 4 structure of pB is 70% or more, and it is the content of a vinyl aromatic series polymer. It is 5 - 50% and the content of pB and pI is a block copolymer which is pB/pI>=1 in a weight ratio,

Phase which uses an organic lithium initiator with a non-active hydrocarbon system solvent, carries out a polymerization until it adds a vinyl aromatic series monomer and a negatively accelerated phosphorescence is carried out, and compounds a living polymerization object;

until it adds an isoprene monomer on the above-mentioned living polymerization object and a negatively accelerated phosphorescence is carried out to it -- a polymerization -- carrying out -- a jib -- phase; which compounds a lock living polymerization object

the above-mentioned jib -- phase; which carries out a polymerization until it adds a butadiene monomer on a lock living polymerization object additionally and a negatively accelerated phosphorescence is carried out to it, and compounds a triblock living polymerization object -- and

It is the manufacture approach of a block copolymer about consisting of phases of adding a binder on the above-mentioned triblock living polymerization object, and carrying out a coupling reaction.
[0020]
It is as follows when it explains in more detail to the manufacture approach which such this invention presents. This invention adds an isoprene polymer block to a vinyl aromatic series monomer and a butadiene block copolymer, and relates to the approach of manufacturing vinyl aromatic series-isoprene-butadiene the copolymer of 3 yuan which raised mechanical physical properties using the solubility constant difference between a vinyl aromatic series polymer and an isoprene polymer.
[0021]
A polymerization will be carried out and it will fully giant-molecule-be made to beized if the polymerization phase of the block copolymer of this invention is explained to a detail until it supplies a vinyl aromatic series monomer and an organic lithium initiator and a negatively accelerated phosphorescence is carried out under a non-active hydrocarbon system solvent as one step ([vinyl aromatic series polymer]-Li). It is styrene most preferably the place which can choose and use one or more sorts as a vinyl aromatic series monomer by this invention out of styrene, alpha-methyl-styrene, o-methyl styrene, p-methyl styrene, p-tert-butyl styrene and 1, and 3-dimethyl styrene. And it can be used, choosing from the solvents usually known as an object for anionic polymerization as a non-active hydrocarbon system solvent for polymerizations. It is being able to use linearity aliphatic hydrocarbon system solvents, such as a cyclohexane or an annular aliphatic hydrocarbon system solvent like a cyclopentane, n-hexane, or n-heptane, etc., and more specifically using the mixture of a cyclohexane, a cyclohexane, and n-hexane, and the mixture of a cyclohexane and n-heptane preferably. Moreover, although it is usually used as an object for anionic polymerization as an organic lithium initiator, it is using n-butyl lithium or sec-butyl lithium preferably the place which can be used choosing from inside. until it adds an isoprene monomer to the above-mentioned giant molecule and a negatively accelerated phosphorescence is carried out to it in two steps -- a polymerization -- carrying out -- a vinyl aromatic series block-isoprene polymer block-Li type jib -- a lock living polymerization object is compounded ([vinyl aromatic series polymer]-[isoprene polymer]-Li). the jib above-mentioned in a three-stage -- a butadiene is added to a lock copolymer and a triblock copolymer is compounded ([vinyl aromatic series polymer]-[isoprene polymer]-[butadiene polymer]-Li). the last coupling phase is throwing in the binder (coupling agent) which has the joint functional group combinable with a living polymerization object anion in response to the above-mentioned triblock copolymer, and manufacturing the block copolymer of 3 yuan [[vinyl aromatic series polymer]-[isoprene polymer]-[butadiene polymer]-[isoprene polymer] - a vinyl aromatic series polymer]. A joint functional group can turn into an anion, a halogen which can react, double association, the Ester radical, etc. The dibromoethane which has two joint functional groups as a binder (dibromoethane), A dihalogen-ized alkane like a dichloroethane (dichloroethane), dibromomethane (dibromomethane), and dichloromethane (dichloromethane), Dichloro JIMECHI rutin (dichlorodimethyltin), Dichloro JIFENI rutin (dichlorodiphenyltin), Dichlorodimethylsilane (dichlorodimethylsilane), There is a dichloro diphenyl silane (dichlorodiphenylsilane). The TORIKURORO methylsilane which has three joint functional groups (trichloromethylsilane), TORIKURORO phenylsilane (trichlorophenylsilane), TORIKUROROMECHI rutin (trichloromethyltin), There is TORIKUROROFENI rutin (trichlorophenyltin) etc. The tetra-chlorosilicane which has four joint functional groups (tetrachlorosilane), A tetrabromo silane (tetrabromosilane), tetra-clo ROCHIN (tetrachlorotin), There is tetra-BUROMOCHIN (tetrabromotin), when it has two or more double association, there is [******] a divinylbenzene (divinylbenzene), and it can be used from this inside, being able to choose one or more. When the binder which has two joint functional groups is used, the block giant molecule of linearity (linear) structure is obtained, and when the binder which has three or more joint functional groups is used, the block giant molecule of radial (radial) structure is obtained.
[0022]
the temperature conditions which are temperature conditions with the same temperature according to each phase of the above-mentioned polymerization reaction, or difference -- which -- possible -- constant temperature -- conditions and heat insulation conditions are all possible. The range of possible reaction temperature is -10-150 degrees C, and is 10-100 degrees C preferably. They are both the contents of vinyl aromatic series before and after a coupling reaction with a 3 yuan block copolymer. Although it is applicable within 5 - 95 % of the weight, for a suitable mechanical strength and an application, that whose content of vinyl aromatic series is 5 - 50 % of the weight is desirable, and it is the thing of the 5 - 35-% of the weight range most preferably. Although the molecular weight of a vinyl aromatic series block

does not need to be a specific value, in order to maintain mechanical physical properties and application physical properties, it is possible in the about 5,000 to 30,000 range, and the range of it is 8,000-20,000 preferably. The molecular weight of the 3 yuan block copolymer after a coupling reaction is possible in 50,000-400,000, and is the thing of 80,000-300,000 preferably. Although the rate of coupling is applicable to less than 10 - 100%, for balance application application, 30 - 100% is desirable, and the most desirable thing is a thing of 50 - 100% range.
[0023]
Hereafter, if an example explains this invention to a detail, it will be as follows and this invention will not be limited by the example.
Example 1
After mixing KISAN 960g and styrene 24g to cyclo to 2L internal pressure reactor under nitrogen-gas-atmosphere mind, 0.0023 mols of n-butyl lithium were added at 60 degrees C, and the reaction was started. 2 minutes after adding isoprene 24g and carrying out a polymerization reaction, 10 minutes after a polymerization reaction's advancing and reaching a maximum temperature, and the polymerization temperature of an isoprene reaching a maximum temperature, the polymerization of the butadiene 112g was added and carried out. 3 minutes after polymerization temperature reached the maximum temperature, 0.001 mols of dichloro methylsilanes were added and the ligation reaction was carried out. Little addition of the methyl alcohol was carried out at the polymer solution by which the polymerization was carried out, the activity of a living polymer was removed completely, and the antioxidant was added. Polymer crumbs (polymer crumb) were collected through the deliquoring process which used steam after that. Polymer crumb was dried using the roll mill (roll mill).
Example 2
Although the polymerization was carried out by the same approach as an example 1, the amount of the isoprene added was set to 40g, and the amount of a butadiene was set to 96g.
Example 3
Although the polymerization was carried out by the same approach as an example 1, the amount of an isoprene was set to 56g and the amount of a butadiene was set to 80g.
The example 1 of a comparison
After mixing KISAN 960g and styrene 24g to cyclo to 2L internal pressure reactor under nitrogen-gas-atmosphere mind, 0.0023 mols of n-butyl lithium were added at 60 degrees C, and the reaction was started. 10 minutes after the polymerization reaction's having advanced and reaching a maximum temperature, butadiene 136g was added and the polymerization reaction was carried out. 3 minutes after the polymerization temperature of a butadiene reached the maximum temperature, 0.001 mols of dichloro methylsilanes were added and the ligation reaction was carried out. Little addition of the methyl alcohol was carried out as a conclusion agent of a polymerization at the living-polymer solution by which the polymerization was carried out, the activity of a living polymer was removed completely, and the antioxidant was added. After obtaining polymer crumb through the deliquoring process which used steam after that, it dried using the 110-degree C roll mill (roll mill).
Example 4
Molecular weight was obtained using GPC (Gel Permeation Chromatography) to the data obtained in examples 1, 2, and 3 and the example 1 of a comparison, and the sheet was manufactured for the polymer dried by the roll mill using the hotpress. The piece of a physical-properties trial of a dumbbell shape was cut from the manufactured sheet, and mechanical physical properties were measured using the tension tester (Instron). The GPC analysis result and the measurement result of tensile strength were expressed to Table 1.
[0024]
[Table 1]

区分	比較例1	実施例		
		1	2	3
スチレン(g)	24	24	24	24
イソプレン(g)	-	24	40	56
ブタジエン(g)	136	112	96	80
イソプレン含量(重量%)	0	15	25	35
分子量(g/mol)	276,000	243,000	279,000	251,000
カップリング率(%)	84	82	69	72
引張強度(kgf/ cm^2)	22	30	93	126
伸率(%)	400	550	1100	1250
300%弾性率(kgf/ cm^2)	18	18.5	18.4	18.2

Although it has low tensile strength, as for the copolymer which consists of a styrene polymer and a butadiene polymer block, it turns out that the tensile strength of a copolymer increases as the content of that an isoprene polymer block is inserted between a styrene polymer and a butadiene polymer block and an isoprene is increased, so that it may see from the conditions of the example of a comparison of the above results.

[0025]

EFFECT OF THE INVENTION

As explained above, by having the structure where the isoprene block-polymer block was inserted between the styrene polymer block and the butadiene polymer block, the copolymer which has the structure by this invention has high tensile strength, and when the content variate of a component makes it possible, it enables suitable physical-properties embodiment by the application.

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TECHNICAL FIELD

[Field of the Invention]
[0001]
This invention relates to a vinyl aromatic series polymer and the block copolymer which has the structure where the isoprene block was added by the butadiene polymer block about the block copolymer which consists of a vinyl aromatic series polymer and a butadiene polymer. The physical-properties embodiment as a thermoplastic elastic body is related with the structure and its manufacture approach of an easy block copolymer by relative content accommodation of a block copolymer in more detail about the block copolymer of the vinyl aromatic series polymer whose mechanical strength improved, and a butadiene polymer.

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PRIOR ART

[Background of the Invention]
[0002]
Generally the styrene system block copolymer (Styrenic Block Copolymer) which consists of a giant-molecule block of a vinyl aromatic series monomer and a conjugated diene giant-molecule block has the structure of 3-fold block or a double block, and has the property of a thermoplastic elastic body. It can be said that SBS (polystyrene-block-polybutadiene-block-polystyrene) obtained when a butadiene is used as an inside [this] conjugated diene monomer is the typical macromolecule of a styrene system block copolymer (SBC, styrenic block copolymer). SBS has 3-fold block structure which consists of a styrene polymer block which is a hard giant molecule, and a butadiene polymer block which is an elasticity giant molecule with high elasticity, and such a structural description offers high application. Two sorts of polymer blocks are not mixed with each other, detailed phase separation is made, and such a phenomenon of a block copolymer is distinguished from the phase separation generated in general macromolecule mixing from the point that between blocks consists of covalent bond. That is, a main block is an elastic body giant molecule, and it will have the configuration connected with the giant-molecule chain of the main block which has elasticity between the strong letters of isolation which the giant-molecule block of both ends forms completely by having the giant-molecule block of the letter of isolation in both. Therefore, this high polymer will have the thermoplasticity and the mechanical strength which the giant molecule which forms the letter of isolation offers, and the elastic body giant molecule which is a main block will have in coincidence the elasticity which can store mechanical stress to a giant-molecule chain. Therefore, SBS is used for wide range applicable fields, such as modified asphalt, compounding, shoes components, and adhesives, as a thermoplastic elastic body which has the property of thermoplastics, and the property of an elastic body in coincidence. On the other hand, SIS (polystyrene-block-polyisoprene-block-polystyrene) of 3-fold block structure acquired from a styrene polymer and an isoprene polymer is mainly used as a material of a binder or adhesives.
[0003]
The block copolymer of various structures is shown about styrene, the butadiene, and the 3 yuan copolymer that consists of an isoprene. It is shown to the American patent No. 3,692,874 about the approach of introducing the block of a butadiene polymer into the block end of an isoprene polymer, and raising coupling effectiveness. Moreover, in No. 5,292,819 and No. 5,399,627, it has shown about the copolymer of the radial structure which appears by the formula of nX (n> 2) (pS-pI-pB). Especially the content of Pb block introduced in order to make coupling smooth has presented 5 or less % of the weight 10 or less % of the weight. If a coupling reaction is carried out for the polymer of an isoprene end by dichlorodimethylsilane under a benzene solvent according to the announced paper (53 JPS vol 36 1743- 1998), it will be reported that 79% of coupling ratio is shown 20 hours after. According to this paper, the steric hindrance effectiveness of a reaction end was taken up as a key factor child who affects a coupling ratio. In the case of the isoprene, the steric hindrance effectiveness by the methyl group of an end interpreted it as it being large and the ratio of coupling being low compared with the butadiene. In this case, in order to raise coupling effectiveness, a little butadiene block is merely added and the overall elastic body effectiveness is acquired from an isoprene block. Therefore, the block copolymer obtained in this way has the physical properties of SIS which consist of a block of a styrene polymer and an isoprene polymer fundamentally.
[0004]
Moreover, in order to raise thermal stability, there is an example which introduced both the isoprene block and the

butadiene block. Generally, since crosslinking reaction occurs at an elevated temperature, viscosity increases a butadiene macromolecule, and if an isoprene macromolecule is heated, viscosity will decrease along with association between atoms being disassembled. Therefore, there is an example shown about the approach which the viscosity change in an elevated temperature is offset and raises thermal stability by introducing both an isoprene block and a butadiene block.

[0005]

In American JP,4,120,915,B, it has shown about the block copolymer which consists of the styrene which appears in S-D1-D2, conjugated diene, and the 2nd conjugated diene. It aims at improvement in thermal stability by introducing both blocks of a butadiene and the conjugated diene which appears in an isoprene. However, since this giant molecule is a resin giant molecule whose styrene content is 70% or more, the improvement in physical properties by such block installation has not been described. Moreover, it is characterized by having the molecular structure of the multiplex branch manufactured using a multiplex coupling agent.

[0006]

According to the American patent No. 5,532,319 and No. 5,583,182, the 3 yuan block copolymer of nX gestalt which introduces a butadiene block into a vinyl aromatic series-isoprene block copolymer, and is formed (S-B-I) was used, and the approach of preventing reduction of the viscosity by time amount at the time of manufacture of hot melt adhesive is shown by raising thermal stability.

[Patent reference 1] The American patent No. 3,692,874
[Patent reference 2] The American patent No. 5,292,819
[Patent reference 3] The American patent No. 5,399,627
[Patent reference 4] The American patent No. 4,120,915
[Patent reference 5] The American patent No. 5,532,319
[Patent reference 6] The American patent No. 5,583,182

[0007]

However, while the research to which research of most which made reference above adds a small amount of [at the end of a vinyl aromatic series-isoprene block copolymer] butadiene for an improvement of a coupling reaction rate and the improvement in thermal stability of a giant molecule at the time of manufacture of a vinyl aromatic series-isoprene block copolymer is most and adjusts the content of a vinyl aromatic series component, use of the isoprene for the mechanical improvement in physical properties of a vinyl aromatic series-butadiene block copolymer is not reported.

[0008]

As for the SBS product which turned quotient business, it is common to have about 30% of the weight of the styrene content. Since a mechanical strength will fall rapidly if there are few styrene contents than this, it can be said that the above-mentioned styrene content is the boundary point to which phase separation can happen effectively since it has a property as a thermoplastic elastic body. However, a styrene content affects mechanical physical properties, such as an index which affects the workability of a block copolymer, such as melt viscosity (melt viscosity) and solution viscosity (solution viscosity), tensile strength (tensile strength), and a degree of hardness (hardness). The material from which change of such physical properties etc. was called for by the application used, therefore the styrene content changed is called for. On the other hand, by SIS for which the isoprene was used instead of the butadiene, since the solubility constant difference between two components is large compared with the case of a vinyl aromatic series-butadiene, the vinyl aromatic series-isoprene block copolymer shows mechanical physical properties with the presentation of a vinyl aromatic series component sufficient [at least about 15 % of the weight]. According to the thermodynamic theory, the phase separation of a block copolymer is based on the common characteristic of the matter to block, the molecular weight of a block copolymer, and the relative content of each component (Hamley, I.W., The Physics of Block Copolymers; Oxford University Press; Oxford, U.K.1998). A common characteristic is determined by the dissolution constant (solubility parameter) difference in the matter which forms a block. These three elements do not act in independent and determine overall phase separation with an interrelation. Therefore, changing the relative content of a component, effectiveness [satisfying / phase separation], i.e., in order to embody the physical properties of a thermoplastic elastic body as a result, it should adjust appropriately so that it may be compensated with the effectiveness by other elements, i.e., common characteristic, and molecular weight. After this invention performed consideration which has depth from such a viewpoint in the thermodynamic variable accompanying the phase separation effectiveness of a block copolymer, and it exerted on phase separation for suitable physical-properties

embodiment, it is obtained.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]
[0009]
The purpose of this invention is for solving the above-mentioned trouble, and it sets it as the purpose to offer the vinyl aromatic series-butadiene block copolymer [mechanical physical properties are excellent, and / relative content accommodation of a block-copolymer constituent is easy, and] which can embody the suitable physical properties accompanying it.

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MEANS

[Means for Solving the Problem]
[0010]
the purpose of above this inventions is 5-fold block copolymer, and appears by the following formula (1) molecular weight is 50,000-400,000 and, for the inside pB of the following formula, 1 and 4 structure is 70% or more -- content of pS It is 5 - 50% and the content of pB and pI is attained by the 3 yuan block copolymer characterized by being pB/pI>=1 in a weight ratio.
pS-pI-pB-pI-pS (1)
However, by the formula, pS is a vinyl aromatic series polymer, pB is a butadiene polymer, and pI is an isoprene polymer.
[0011]
The block copolymer which this invention presents is characterized by having embodied the property as a thermoplastic elastic body whose mechanical physical properties has the structure of a 3 yuan block copolymer of the structure where the isoprene polymer block was added between the vinyl aromatic series polymer block and the butadiene polymer block, and improved according to the solubility constant difference between a vinyl aromatic series component and an isoprene polymer.

[Translation done.]